DIMETHYL SULFIDE-DIMETHYL ETHER AND ETHYLENE OXIDE-ETHYLENE SULFIDE COMPLEXES INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION

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The ground-state rotational spectra of the dimethyl sulfide-dimethyl ether (DMS-DME) and the ethylene oxide and ethylene sulfide (EO-ES) complexes were observed by Fourier transform microwave spectroscopy, and a-type and c-type transitions were assigned for the normal, ^{34}S, and three ^{13}C species of the DMS-DME and a-type and b-type rotational transitions for the normal, ^{34}S, and two ^{13}C species of the EO-ES. The observed transitions were analyzed by using an S-reduced asymmetric-top rotational Hamiltonian. The rotational parameters thus derived for the DMS-DME were found consistent with a structure of $C_{\rm s}$ symmetry with the DMS bound to the DME by two C-H(DMS)—O and one S—H-C(DME) hydrogen bonds. The barrier height V_3 to internal rotation of the "free" methyl group in the DME was determined to be 915.4 (23) $\rm cm^{-1}$, which is smaller than that of the DME monomer, 951.72 (70) $\rm cm^{-1}$,[a] and larger than that of the DME dimer, 785.4 (52) $\rm cm^{-1}$.[b] For the EO-ES complex the observed data were interpreted in the terms of an antiparallel $C_{\rm s}$ geometry with the EO bound to the ES by two C-H(ES)—O and two S—H-C(EO) hydrogen bonds. We have applied a natural bond orbital (NBO) analysis to the DMS-DME and EO-ES to calculate the stabilization energy CT (= $\Delta E\sigma\sigma^*$), which were closely correlated with the binding energy $E_{\rm B}$, as found for other related complexes.

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[a] Y. Niide and M. Hayashi, *J. Mol. Spectrosc.* **220**, 65-79 (2003).

[b] Y. Tatamitani, B. Liu, J. Shimada, T. Ogata, P. Ottaviani, A. Maris, W. Caminati, and J. L. Alonso, *J. Am. Chem. Soc.* **124**, 2739-2743 (2002).